

## Reviewers' Comments:

### Reviewer #1 (Remarks to the Author)

The authors present a Raman study of controlled functionalization of graphene, revealing several new bands appearing in the D-region of the spectrum. Evolution of these bands as functionalization is increased from low to moderate levels provides a basis for deconvolution of components towards quantifying the extent of functionalization. The low-level functionalization results are especially useful in that they provide sufficiently discrete spectral features that they can be compared to complementary DFT calculations identifying specific modes associated with the different functionalization sites. This is an important breakthrough and long sought-after goal for Raman spectroscopy of these materials. The ability the authors show to generate model spectra and then quantify contributions will be of significant utility for characterization of graphene and other nanocarbons (single and multiwalled carbon nanotubes, graphene oxide, etc.) as well. The complex spectra of Figure 3 likely have been encountered by a large number of researchers in their characterization efforts, and the author's work is an important step towards improved understanding of how the various features arise. This work should therefore be of both fundamental interest and significant practical use for a large number of researchers and I can recommend publication in Nature Communications after the following concerns are addressed.

1) On page 9 the authors state the calculated phonon frequencies perfectly match the experimental values. This claim is overstated. Values in Tables S1 and S2 don't appear to correlate directly to any of the experimental values at low or moderate functionalization levels. Furthermore the tabulated values don't appear to match up well with the calculated spectra shown in Figure 2. The authors should clarify this apparent disconnect between the tabulated values and both experimental and calculated spectra. It might be useful to consider adding the specific experimental values to the tables so the reader can see the one-to-one correspondence that the authors claim.

2) Minor point: On page 9, line 248, the authors refer to Figure S8. This should be S9.

### Reviewer #2 (Remarks to the Author)

The major achievement of the paper is to detect several new features in the D-modes of the Raman spectra during the early stages of graphene hydrogenation process. Also, the observed features are assigned to distinct lattice vibrations near the covalently bound addend using quantum mechanical calculations. The novelty in this work is the precise detection of covalent bond formation in functionalized graphene materials. In-situ measurements are crucial for understanding reaction mechanisms, hence this technique has a potential to influence a wide range of graphene related research.

The conclusions in the paper are well-justified with the reported data. The methodologies used are convincing to me. Sufficient details are provided to reproduce the results.

I recommend to publish this article after a few minor clarifications.

1. In Fig. 1., deconvolution of the experimental Raman spectra is crucial. It was not clear to me how the deconvolution was done. Were the calculated vibration modes used in the deconvolution?

2. In-situ Raman measurement on graphene related materials is not new and the authors have cited many such previous studies (Ref. 28, 29, for example). It seems each measurement has its own novelty. How transferable the current experimental set up is to study a different system (graphene related or beyond) given that a specific reaction is used here to detect the covalent

bond.

3. I could not find the definition of the phrase "TG/MS" in the paper.

Reviewer #3 (Remarks to the Author)

The manuscript by Vecera et al. "The First Precise Determination of Graphene Functionalisation by in situ Raman Spectroscopy" reports the use of Raman spectroscopy to study the covalent modification of graphene. The manuscript treats a very important topic in the graphene research and particularly graphene chemistry. Expanding the tools for analysis of covalently modified graphene materials beyond the traditional analytical techniques (which have found limited application) is a timely effort and one that will be of interest to researchers in the field. I recommend publication after minor revision to address several questions:

1. Title – from the title the referees was under the impression that this study addresses also quantitative analysis of functionalized graphene materials. I suggest that the authors consider a title which matches more closely the presented qualitative Raman analysis, specifically the assignment of the five D-band modes to distinct lattice vibrations in the covalently modified graphene lattice, which is the main novelty in this manuscript.
2. Band widths of the Raman peaks are not discussed and for complete understanding of the presented analysis this information needs to be presented. Especially because the band width depends on the degree of functionalisation.
3. The authors claim that the concept was used to simulate and characterise additional covalently functionalised graphene derivatives prepared as bulk materials with different composition (e.g. DOF and nature of covalent addend) demonstrating the generality of the method. The only other functionalisation that was included is aryl functionalization in the supporting information, and it is not discussed in the text. For example how was  $\theta$  determined in the examples presented in Figure S10; reference to citation [10] did not help answering this question.
4. Different labelling is used in the figures and throughout the manuscript – D1-D5, CA-CB...., D''', D'' and D'. It is a bit difficult for the reader to follow the discussion and requires reference to multiple figures to understand the discussion.
5. Labelling of the panes of Figure S7 needs to be corrected to reflect to figure caption.

Note: If unpublished work is cited it should be provided to the referees to assure smooth review process. I was not able to understand (nor evaluate) any statements related to reference 30.

## Manuscript No. NCOMMS-16-27166 – Point-by-point Reply to the Referees

### **Reviewer #1 (Remarks to the Author):**

The authors present a Raman study of controlled functionalization of graphene, revealing several new bands appearing in the D-region of the spectrum. Evolution of these bands as functionalization is increased from low to moderate levels provides a basis for deconvolution of components towards quantifying the extent of functionalization. The low-level functionalization results are especially useful in that they provide sufficiently discrete spectral features that they can be compared to complementary DFT calculations identifying specific modes associated with the different functionalization sites. This is an important breakthrough and long sought-after goal for Raman spectroscopy of these materials. The ability the authors show to generate model spectra and then quantify contributions will be of significant utility for characterization of graphene and other nanocarbons (single and multiwalled carbon nanotubes, graphene oxide, etc.) as well. The complex spectra of Figure 3 likely have been encountered by a large number of researchers in their characterization efforts, and the author's work is an important step towards improved understanding of how the various features arise.

This work should therefore be of both fundamental interest and significant practical use for a large number of researchers and I can recommend publication in Nature Communications after the following concerns are addressed.

We are very thankful for the reviewer's comments, suggestions, and the time he invested to review our manuscript. We are very pleased about the very positive feedback of the referee, especially, that the significance and the interest of our study were emphasized and that he recommends the publication of our study in Nature Communications after minor revision.

1) On page 9 the authors state the calculated phonon frequencies perfectly match the experimental values. This claim is overstated. Values in Tables S1 and S2 don't appear to correlate directly to any of the experimental values at low or moderate functionalization levels.

Furthermore the tabulated values don't appear to match up well with the calculated spectra shown in Figure 2. The authors should clarify this apparent disconnect between the tabulated values and both experimental and calculated spectra.

Table S1 lists the calculated phonon frequencies for pristine graphene, the hydrogenated graphene (G-H), and hydroxylated derivative (G-OH). In Table S2 a graphical representation of

the calculated vibrational modes is given. Therefore, our statement given on page 9 “The calculated phonon frequencies (Table S1 and S2) perfectly match the experimental values” may be misleading and in the revised version of the manuscript the statement is only referred to Table S1).

The calculated Raman spectra for **G-H** and **G-OH** are depicted in Figure 2d. The measured experimental spectrum obtained after the exposure of  $\text{KC}_8$  to water is given in Figure 1c and 1d with the corresponding fitted components (G-mode, D-mode, and  $D_1 - D_5$ ). The value of the calculated  $\text{sp}^2$  C=C mode ( $1574 \text{ cm}^{-1}$  for **G-H** and  $1576 \text{ cm}^{-1}$  for **G-OH**) – Figure 2d / Table S1 – perfectly matches the fitted peak position of the G-mode in the functionalized sample ( $1575 \text{ cm}^{-1}$ ) – Figure 1d. This is also the case for the calculated phonon frequency for the  $\text{C}_A\text{-C}_B$  vibration and the experimentally found value for the respective  $D_1$  ( $D''$ ) mode. With respect to the approximations made in the calculation, the limitations provided by the experimental setup (resolution of the detector and calibration ambiguity), and the fact that the covalently functionalized graphene sample is a mixture of hydroxylated and hydrogenated species with varying content the matching between the calculated and experimental values for the evolving bands in the region between  $1325 \text{ cm}^{-1}$  ( $D_1 / D''$ ) and  $1559 \text{ cm}^{-1}$  ( $D_5 / D'$ ) is in our opinion also significant.

Nevertheless, in the revised version of the manuscript we softened our statement to “is in good correlation” and have also specified the limiting factors given above.

*It might be useful to consider adding the specific experimental values to the tables so the reader can see the one-to-one correspondence that the authors claim.*

In line with the helpful suggestion of the referee we have revised Table S1 and added the determined experimental values in order to clarify the correlation between the calculated values and the experimental data determined from the *in situ* spectra of Figure 1d.

2) Minor point: On page 9, line 248, the authors refer to Figure S8. This should be S9.

We thank the reviewer for his kind attention. The right reference to Figure S9 is provided in the revised version of the manuscript.

**Reviewer #2 (Remarks to the Author):**

*The major achievement of the paper is to detect several new features in the D-modes of the Raman spectra during the early stages of graphene hydrogenation process. Also, the observed features are assigned to distinct lattice vibrations near the covalently bound addend using quantum mechanical calculations. The novelty in this work is the precise detection of covalent bond formation in functionalized graphene materials. In-situ measurements are crucial for understanding reaction mechanisms, hence this technique has a potential to influence a wide range of graphene related research.*

*The conclusions in the paper are well justified with the reported data. The methodologies used are convincing to me. Sufficient details are provided to reproduce the results.*

*I recommend to publish this article after a few minor clarifications.*

We kindly thank the reviewer for this very positive feedback and appreciate his detailed analysis, comments and suggestions for an improvement of the manuscript.

1) In Fig. 1., deconvolution of the experimental Raman spectra is crucial. It was not clear to me how the deconvolution was done. Were the calculated vibration modes used in the convolution?

We apologize for any confusion related to our use of the term “deconvolution”. In our case, a line shape analysis of the different components with voigtians including resolution and life time broadening has been carried out. This yields the fingerprint of the individual components and modes. The theory calculates a phonon pattern which after resolution and life time broadening should match the shape of the experimental spectra and can be used to assign the individual components/modes in the fingerprint region, which allows an unambiguous assignment of the components. The strength of the *in situ* experiments is that we are able to experimentally calibrate our spectra using different trapping reagent concentrations to get a quantitative measure for the degree of functionalization in the medium to high covalent graphene functionalization regime.

In detail, the line-shape analysis performed in Figure 1d was carried out with the first objective of identifying the amount of vibrational modes present in the final functionalized material. At this point, the theoretical description was still not introduced in the analysis – this may have lead to a misunderstanding. Nevertheless, the assignment of each known fitted component in Figure 1d was addressed to different experimental literature values. The up to now undetected modes ( $D_1$  to  $D_5$ ) were assigned to the presence of vibrational modes in the direct neighbourhood of the  $sp^3$  hybridized C lattice atom bearing the covalently attached hydrogen/hydroxyl moieties, while their deconvolution and precise assignment was demonstrated in Figure 2 c-d.

In order to avoid any confusion, we have clarified this point and rephrased the respective paragraph in the revised version of the manuscript.

2. *In-situ Raman measurement on graphene related materials is not new and the authors have cited many such previous studies (Ref. 28, 29, for example). It seems each measurement has its own novelty. How transferable the current experimental set up is to study a different system (graphene related or beyond) given that a specific reaction is used here to detect the covalent bond.*

In principle, the referee addresses a very fundamental question. He is right, the definition “*in situ* Raman spectroscopy” is used in a wide sense in literature. In our case, the term is used for the spectroscopic monitoring of a chemical derivatization of highly reactive graphite intercalation compound by Raman spectroscopy. This is a very challenging task as completely inert conditions (vacuum or argon atmosphere) are needed for the functionalization/spectroscopic investigation. Therefore, a special setup was needed which enabled us to handle the highly reactive starting material and simultaneously gave us the opportunity to apply a trapping reagent with an *in situ* monitoring of the evolution of the distinct Raman modes during the chemical reaction. This unique setup is highly versatile and can easily be applied for other highly reactive 1D- and 2D materials (i.e. black phosphorous, intercalated transition metal dichalcogenides,...) and a broad variety of potential trapping reagents.

In principle, the observed modes in the Raman spectrum are in first order valid for two-dimensional  $sp^2$  systems (extended  $\pi$ -systems larger than  $100 \mu m^2$ ). The question if other Raman active materials show comparable features during the reaction can now easily be tackled by the application of this *in-situ* monitoring setup and is currently under investigation in our lab. Here, other parameters (i.e. laser excitation energy, stability towards the applied laser power, ...) and their influence can easily be investigated.

3. I could not find the definition of the phrase “TG/MS” in the paper.

We would like to apologize that we did not provide the explanation of this abbreviation. TG/MS stands for “thermogravimetric analysis coupled to mass spectrometry” and we have now added that explanation to the revised version of our manuscript.

**Reviewer #3 (Remarks to the Author):**

*The manuscript by Vecera et al. "The First Precise Determination of Graphene Functionalisation by in situ Raman Spectroscopy" reports the use of Raman spectroscopy to study the covalent modification of graphene. The manuscript treats a very important topic in the graphene research and particularly graphene chemistry. Expanding the tools for analysis of covalently modified graphene materials beyond the traditional analytical techniques (which have found limited application) is a timely effort and one that will be of interest to researchers in the field. I recommend publication after minor revision to address several questions.*

We highly appreciate the time and effort that the referee has invested to review our presented work and we are very pleased about his positive feedback and his recommendation to publish our manuscript after his minor revision points have been addressed.

1. Title – from the title the referees was under the impression that this study addresses also quantitative analysis of functionalized graphene materials. I suggest that the authors consider a title which matches more closely the presented qualitative Raman analysis, specifically the assignment of the five D-band modes to distinct lattice vibrations in the covalently modified graphene lattice, which is the main novelty in this manuscript.

We agree with the reviewer that the manuscript is not primarily focused on the quantification of the functionalization extent of graphene. Nevertheless, this topic is fundamentally interconnected to the changes in  $sp^2$  carbon lattice in the course of the functionalization and this is exactly addressed by our presented Raman *in situ* investigation. In addition, the strength of the *in situ* experiments is that we are able to experimentally calibrate our spectra using different trapping reagent concentrations to actually get a quantitative measure for the degree of functionalization in the medium to high covalent graphene functionalization regime. In our opinion these facts justify the chosen title of the manuscript, where the term "precise" which not solely is correlated with quantification but also with a qualitative assignment of the new evolving bands in the course of the covalent functionalization of graphene.

The direct correlation between the functionalization induced Raman intensity changes and the quantification of the degree of functionalization has been addressed by us in a different manuscript (reference 30) submitted to Scientific Reports (will be published after minor revision). The referee has already mentioned that had no access to this reference and we would like to apologize for this fact. Therefore, we kindly provide the submitted version of that manuscript to the reviewer. The presented results therein will help to answer some open questions raised.

Our findings show, that the for a quantitative determination of a degree of functionalization in virtually any graphene derivative the sum of all individual components (= overall intensity) in the

Raman signal has to be taken into account. In connection to the manuscript submitted to Nature Communications, both methods complementarily provide the entire information about the qualitative (present manuscript) and quantitative (Sci. Rep. ref. 30) analysis of functionalized graphene.

*2. Band widths of the Raman peaks are not discussed and for complete understanding of the presented analysis this information needs to be presented. Especially because the band width depends on the degree of functionalisation.*

In principle, the reviewer is right that the band width depends on the degree of functionalization, which is another fact that has to be considered in the analysis of the Raman spectra of functionalized graphene. The presented work focusses on the evolution of new Raman bands, directly related to a change of the phonon mode frequencies of lattice carbon atoms in close proximity to the introduced  $sp^3$  center. Since the evolution of the additional defect induced modes  $D_1$ - $D_5$  and the broadening of the D- and G-mode appear simultaneously, we developed a systematic model which considers the overall intensity in the Raman spectrum. With this approach, all spectral changes are determined, which is also described in our ref. 30. As stated, above, we kindly provide the submitted version of that manuscript to the reviewer.

*3. The authors claim that the concept was used to simulate and characterise additional covalently functionalised graphene derivatives prepared as bulk materials with different composition (e.g. DOF and nature of covalent addend) demonstrating the generality of the method. The only other functionalisation that was included is aryl functionalization in the supporting information, and it is not discussed in the text. For example how was  $\theta$  determined in the examples presented in Figure S10; reference to citation [10] did not help answering this question.*

Again we have to apologize that the reviewer had no access to ref. 30 and we would like to thank the reviewer for bringing our attention to this inconsistency in the manuscript. At the very low stage of functionalization, any type of  $sp^3$  defect can be considered as isotropically distributed point defect and therefore the additional defect modes  $D_1$ - $D_5$  are not visible in the Raman spectrum at this stage. Thus, the signature of the addend in Raman spectroscopy is independent of its nature at these low stages of DOF. The synthesis of the aryl functionalized sample was adapted from literature and used within both reference [10] and ref. [30] from our recent work. To clarify that point within this manuscript, we provided additional experimental details in the revised version of the supplementary information.



4. Different labelling is used in the figures and throughout the manuscript – D1-D5, CA-CB..., D''', D'' and D'. It is a bit difficult for the reader to follow the discussion and requires reference to multiple figures to understand the discussion.

We agree with the reviewer that the labelling might be confusing at the first glance. We have already thought about a more general labelling, however, the described modes are different and have to stay labelled differently: Starting from the modes observed *in situ* (= charged sample under inert conditions) we labeled the experimentally found novel modes with D<sub>1</sub>-D<sub>5</sub>, while the calculations revealed distinct vibrations of lattice carbon atoms (C<sub>A</sub>-C<sub>B</sub> and so forth) which can be related to the previous ones. Finally, under ambient conditions and high DOFs, the situation is again different and requires another termination (D''', etc.). We tried to clarify this relation by summarizing the respective information in the revised version of the supplementary Table S1.

5. Labelling of the panes of Figure S7 needs to be corrected to reflect to figure caption.

To the best of our knowledge the labelling of the figures and the caption text in Figure S7 is correct.

*Note: If unpublished work is cited it should be provided to the referees to assure smooth review process. I was not able to understand (nor evaluate) any statements related to reference 30.*

The reviewer is totally right and we are sorry for not being able to provide a published version of our article which might be important for the entire understanding. As already mentioned, the reviewer should now have access to this information.

Reviewers' Comments:

Reviewer #1 (Remarks to the Author)

I have reviewed the revised manuscript and the response to all reviews. I believe the authors have addressed the review comments appropriately and have made the necessary revisions to the manuscript. I can recommend this be published in Nature Communications in its current form.

Reviewer #2 (Remarks to the Author)

The author's response letter and the corrections made to the manuscript are satisfactory to me. I recommend for publication of the article in Nature Communications.

Reviewer #3 (Remarks to the Author)

The authors have addressed all questions raised by the reviewers. I recommend the revised manuscript for publication.